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Abstract

The thermal degradation of polystyrene, high-impact polystyrene, ABS terpolymer, poly(methyl methacrylate), polypropylene and polyethylene nanocomposites has been studied using thermogravimetric analysis coupled to Fourier transform infrared spectroscopy, TGA/FT-IR. The nanocomposites that have been studied include immiscible, intercalated and exfoliated systems and the evolved gases do not depend upon the type of nanocomposite and are qualitatively similar to those of the virgin polymer. In the case of the styrenics, the presence of clay promotes the production of oligomer, rather than monomer. It is suggested that this change in evolved products may offer an explanation for why some polymers give large reduction in peak heat release rates while others give much smaller reductions. According to this notion, any polymer that undergoes degradation to produce both oligomer and monomer should give a large reduction in peak heat release rate.

Keywords

Nanocomposites, TGA/FTIR, Polystyrene

1. Introduction

The addition of a small amount of clay to a polymer produces a nanocomposite, which has enhanced properties relative to those of the virgin polymer. In particular, the flexural modulus, fire retardancy, heat distortion temperature and permeability all show improvement. There are three types of nanocomposites, immiscible (also known as a microcomposite) in which the clay is not well-dispersed, intercalated, in which the registry between the clay layers is maintained and exfoliated (also known as delaminated) in which the registry between the clay layers is lost. The type of nanocomposite is important for some purposes, particularly permeability and flexural modulus for which the exfoliated system appears to give the best results, but for fire retardancy there appears to be no difference between intercalated and exfoliated systems.

The preparation of nanocomposites may be accomplished by either a polymerization process or a blending process. While polymerization processes are very useful on the laboratory scale, it is likely that melt blending is the method of choice for the industrial situation. The thermal stability of the clay, and especially its organic counterion, becomes an important issue for nanocomposite formation. We have recently reported two new, thermally stable, clay treatments that afford the opportunity for melt blending with a wide variety of polymers, including polystyrene and its copolymers, poly(methyl methacryalte), and the polyolefins, polyethylene and polypropylene. This new clay treatment involves the preparation of an oligomeric styrene (COPS) or an oligomeric methacrylate (MAPS) unit that can be attached to an ammonium salt and then this salt is attached to the clay. In contrast to the usual ammonium counterions used with clays, that undergo thermal degradation beginning near 200 °C, this new clay shows substantially enhanced thermal stability and has only lost less than 7% of its mass at 350 °C.

In this paper we examine the thermal stability of COPS and MAPS clays and their nanocomposites with polystyrene (PS), high impact polystyrene (HIPS), acrylonitrile-butadiene-styrene terpolymer (ABS), poly(methyl methacrylate) (PMMA), polypropylene (PP) and polyethylene (PE) by TGA/FTIR.

2. Experimental

2.1. Materials

The majority of chemicals used in this study, including vinylbenzyl chloride, styrene, benzoyl peroxide(BPO), N,N-dimethylhexadecylamine, initiator removal reagents, PS (melt flow index 200 °C/5 kg, 7.5 g/10 min, Mw=230,000), HIPS (melt flow index 200 °C/5 kg, 6 g/10 min), PMMA (crystals, Mw=996,000 (GPC), inherent viscosity 1.25), PE (melt flow index,190 °C/2.16 kg, 7 g/10 min), PP (Isotactic, melt flow index,230 °C/2.16 kg, 35 g/10 min) were acquired from Aldrich Chemical Co. ABS (Magnum 275, 230 °C/3.8 kg, 2.6 g/10 min) was acquired from Dow Chemical Co. Pristine sodium montmorillonite was provided by Southern Clay Products, Inc.

2.2. Instrumentation

TGA/FTIR studies were carried out using a Cahn TG131 thermogravimetric analyzer that was interfaced to a Mattson Research grade Fourier transform infrared spectrometer at a scan rate of 20 °C per minute under a flowing nitrogen atmosphere. All runs have been performed in duplicate. Carbon dioxide is ubiquitous in TGA/FTIR studies and bands from this material are ignored in this analysis.

The preparation and characterization of the nanocomposites have been previously described.

3. Results and discussion

This study reports on the thermal stability of two clays, both of these have been produced by the ion-exchange of sodium montmorillonite with ammonium salts. This is an essential treatment in order to make the clay sufficiently organophilic to enable the organic polymer to insert between the clay layers. Both of these new clays contain two methyl groups, one hexadecyl group and another, oligomeric group; it is this last group which enhances the thermal stability of the clay and, ultimately, of the nanocomposites. These two oligomeric groups contain either styrene (COPS) or methyl methacrylate (MAPS), with a molecular weight of about 5000; in order to enable the attachment of these units to the nitrogen, these oligomers also contain about 5% vinylbenzyl chloride. This last material permits the facile quaternization of an amine to give an ammonium salt.

We have previously reported the X-ray diffraction, transmission electron microscopy, thermogravimetric analysis, cone calorimetry and mechanical properties of these materials [1], [2]. According to the X-ray diffraction and transmission electron microscopy, the COPS system gives good nanodispersion with all polymers that have been studied and the nanocomposites may be best described as mixed intercalated/exfoliated systems. On the other hand, MAPS, in general, does not give such good nanodispersion and there is a definite immiscible component to all of the MAPS systems. Further studies on thermal stability are carried out using thermogravimetric analysis coupled to Fourier transform infrared spectroscopy, TGA/FTIR. This technique has been shown in previous studies to be very useful in probes of thermal stability because one can identify the products of the degradation and thus better understand the degradation pathway.

3.1. Thermal degradation of COPS and MAPS clays

Fig. 1 shows the infrared spectra of the COPS-modified clay as a function of the temperature at which the volatiles are evolved. Since this clay contains styrene, one may expect to see materials that arise from the degradation of polystyrene. The thermal degradation of styrene has been studied by several workers [3], [4], [5], [6], [7], [8]. The degradation commences at about 360 °C and is complete by 450 °C; it occurs by both end chain and random scission and the products that are produced are styrene monomer and oligomer, along with benzene and toluene. In this study we find that the degradation commences at a lower temperature, 275 °C, where there is 2% degradation. The only peaks observed are those in the aliphatic C–H stretching frequency region, below 3000 cm^{-1}, indicative of the evolution of the hexadecyl group. It is known from previous work with various ammonium cations in the clay that the long alkyl chains undergo the initial degradation, by a Hofmann elimination process, to give an olefin [9], [10]. When the temperature is increased to 320 °C, the presence of a weak peak in the aromatic C–H stretching frequency region, above 3000 cm^{-1} can be seen and this is indicative of the beginning of the degradation of the styryl group. At 470 °C, one can see the presence of styrene oligomers, due to a peak near 1600 cm^{-1}. It is known that the degradation of polystyrene proceeds by the elimination of both monomer and oligomers of styrene; the monomer absorbs at 1630 cm^{-1} [11]. The assignment of the oligomer peak at 1600 cm^{-1} may be seen by comparison of the spectra of compounds such as 1,4-diphenyl1,3-butadiene, 1,1 diphenylethylene and triphenylethylene [12]. This peak in polystyrene occurs at 1601 cm^{-1}. It is surprising to observe that only the oligomer peak is observed and that monomer appears to be absent.

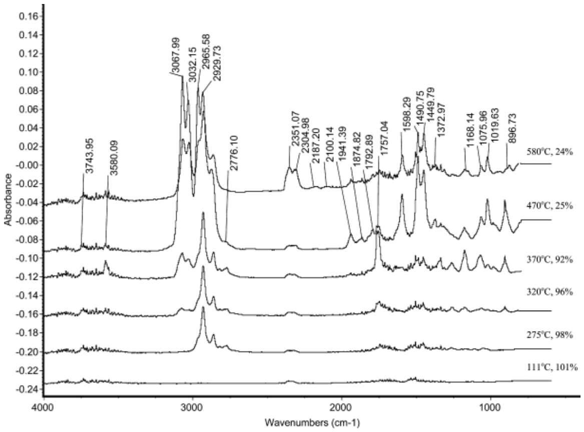

Fig. 1. FT-IR spectra for the TGA/FTIR study of COPS modified clay.

One can compare the spectra of the COPS nanocomposite with that of pure polystyrene, shown in Fig. 2. The first appearance of aromatic C–H in the degradation of PS is at about 380 °C, higher than that observed in COPS clay. The lower stability of the clay may be attributed to the thermal instability of the nitrogen–carbon bond, leading to the more facile loss of the styrene unit. It is of interest to note that peaks at both 1600 and 1630 cm^{-1} are seen for PS, while only the oligomer is seen for the COPS clay. Either monomers combine to form oligomer or monomer does not form. It seems more likely to suggest that the presence of the clay has an influence on the degradation and prevents the formation of monomer. Further work is required to identify why there should be this difference.

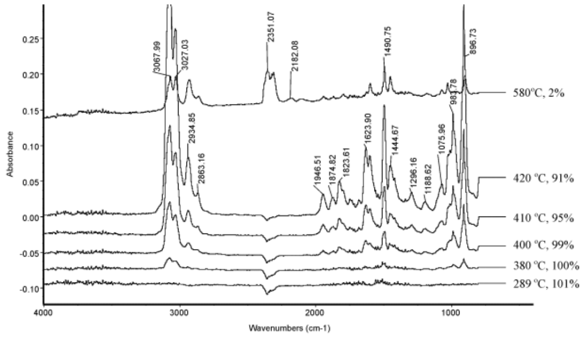

Fig. 2. FT-IR spectra in a TGA/FTIR study of virgin polystyrene.

The infrared spectra of MAPS clay are shown in Fig. 3. The degradation of methyl methacrylate proceeds by an end-chain scission process, leading to the formation of only monomer. Kashiwagi et al. [13] have shown that a radically polymerizerd sample degrades in three steps, around 165, 270 and 360 °C, while an anionically-polymerized sample undergoes only a single degradation step, at 360 °C. They have suggested that the first two steps may be due to the presence of head-to-head linkages and the presence of unsaturated chain ends, respectively, while the degradation at 360 °C is attributed to random scission. In this study, it was found that degradation commences at 250 °C with the evolution of monomeric methyl methacrylate, as seen by the C–H stretching frequency and the carbonyl band. It should be noted that aromatic C–H peaks appear near 275 °C and these must be attributable to the loss of the vinylbenzyl units that are attached to the clay. The fact that these units appear so early may indicate that the site at which degradation is initiated is that which is attached to the nitrogen, where the Hofmann elimination will occur. Even at 500 °C, one can still see the carbonyl band, indicating that the clay is still undergoing degradation. At this temperature for virgin poly(methyl methcarylate), there is no longer any gas evolution. The MAPS clay has enhanced thermal stability compared to PMMA. It is noteworthy that by 300 °C 10% of the clay has been lost while for the COPS clay at this same temperature, only 3% has been lost. It is interesting to note that the degradation occurs in a step-wise fashion, even at 10° or 20 °C per minute. In the work of Kashiwagi, it was necessary to slow the ramp rate to 2 °C per minute to see the individual steps. In previous work from this laboratory on PMMA nanocomposites [14], multiple steps in the PMMA degradation have been seen. It is clear that the presence of the clay has a significant effect on the degradation pathway. Blumstein has studied the polymerization of methyl methacrylate by adsorption onto montmorillonite clay [15], [16], [17], [18], [19], [20]. He suggested that the clay exerted a "memory effect" on the polymerization process and that this led to a tacticity that was not atatic. It is most likely that a similar effect is operative here and that the clay in some way serves as a template to control the pathway of the degradation.

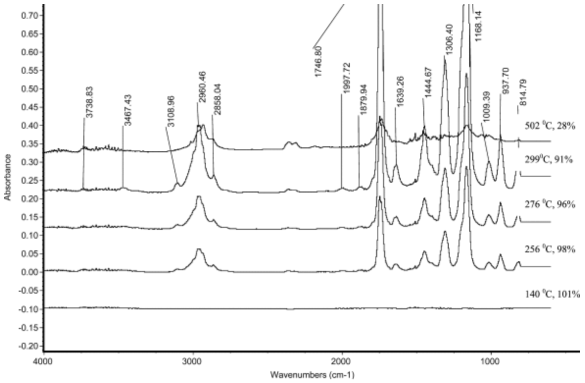

Fig. 3. FT-IR spectra for a TGA/FTIR study of for MAPS modified clay.

3.2. The thermal degradation of polystyrene and its COPS and MAPS nanocomposites

The TGA curves for PS and both nanocomposites are shown in Fig. 4; it is obvious that the COPS–PS nanocomposite degrades at higher temperature, the expected behavior for an intercalated or exfoliated nanocomposite, and that the MAPS–PS system, which is mostly immiscible, degrades at lower temperatures than does virgin PS. The infrared spectra of the COPS–PS nanocomposite are shown in Fig. 5. This material may be slightly less stable than is virgin PS. Unlike COPS clay, the first peak that is seen is aromatic C–H and not the aliphatic. Apparently the small amount of clay, and hence the smaller amount of hexadecyl units, cannot be seen. Again it appears that the formation of oligomers, rather than monomers, is favored in the nanocomposite.

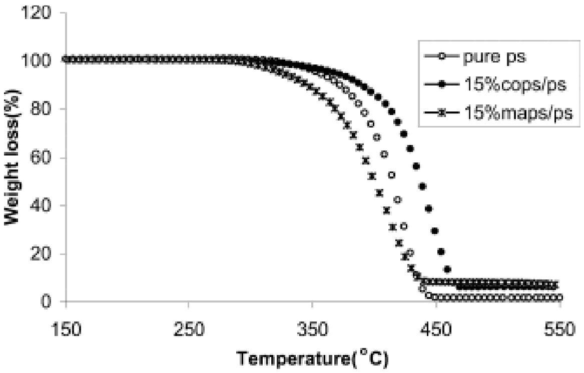

Fig. 4. TGA curves for polystyrene and its COPS and MAPS nanocomposites.

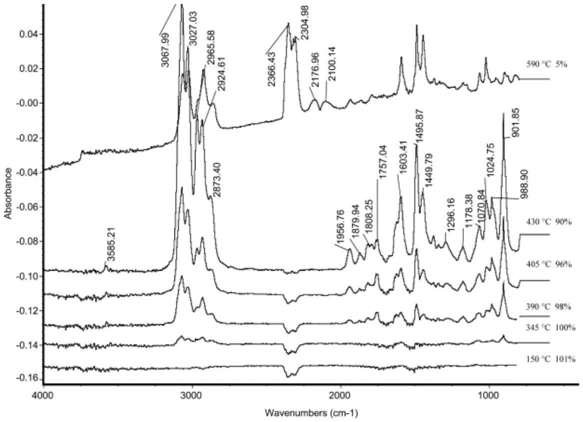

Fig. 5. FT-IR spectra from a TGA/FTIR study of COPS/PS nanocomposite.

The IR traces for MAPS–PS are shown in Fig. 6. The initial degradation is the loss of methacrylate; this is followed by the loss of styrene oligomers beginning at about 385 °C. Even at 585 °C some of the methacrylate from the clay is still evident. Thus this clay does begin to degrade at low temperatures but it does not degrade as easily as does poly(methyl methacrylate). Once again the formation of oligomer, rather than monomer, is favored. There is a difference in the TGA curves for PS and its nanocomposites but the only difference in the evolved gases is the formation of oligomer, rather than monomer and oligomer, from the nanocomposites. COPS–PS is an exfoliated nanocomposite while MAPS–PS is a microcomposite and there is no difference in the evolved gases, including the preference for oligomer, for these two systems. The extent of nano-dispersion, low in the MAPS system and high in the COPS system, does not influence the degradation pathway.

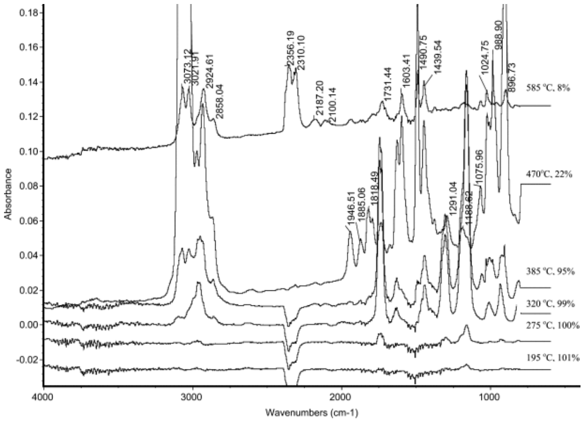

Fig. 6. FT-IR spectra from a TGA/FTIR study of MAPS/PS nanocomposite.

3.3. Thermal degradation of HIPS and its COPS and MAPS nanocomposites

The infrared traces for the degradation of HIPS are shown in Fig. 7. The onset of the thermal degradation occurs at about the same point as seen for PS; the one difference is the presence of a larger aliphatic than the aromatic C–H frequency. Both oligomeric and monomeric styrene units are seen. The TGA curves for virgin HIPS and the nanocomposites are shown in Fig. 8; the onset of degradation occurs earlier in the MAPS system, presumably because of the instability of the methacrylate, and at higher temperatures for COPS–HIPS. It is of interest to note that the curve for MAPS–HIPS does cross that of virgin HIPS and the nanocomposite becomes more thermally stable above about 50% degradation, probably because at this stage the methacrylate is lost.

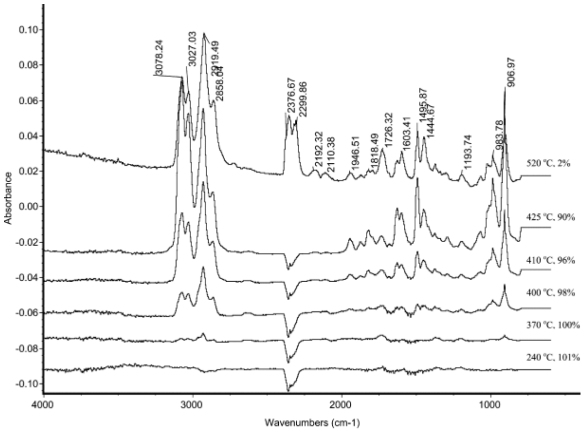

Fig. 7. FT-IR spectra from a TGA/FTIR study of virgin HIPS.

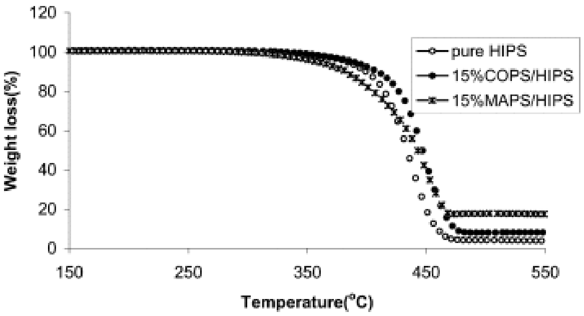

Fig. 8. TGA curves for HIPS and its COPS and MAPS nanocomposites.

In the presence of both COPS clay (Fig. 9) and MAPS clay (Fig. 10), there is little change in the infrared spectra. The first appearance of the C–H stretching frequency for both nanocomposites is about 400 °C. The onset of the degradation for MAPS–HIPS occurs at much lower temperature, 210 °C is the first appearance of infrared bands, but these are due to the methacrylate carbonyl band and thus are attributable to clay degradation and not to degradation of the HIPS. In the case of the COPS–HIPS system, only oligomer, by the peak near 1600 cm^{-1}, is observed until one reaches 510 °C when only 7% of the material remains and now a peak due to monomer at 1630 cm^{-1} can be seen. The spectra for MAPS–HIPS are ambiguous, because the degradation in the early stages is dominated by clay degradation, and one cannot observe either of these peaks. It is of interest to note that COPS–HIPS is an intercalated nanocomposite while MAPS–HIPS is a microcomposite. Neither the presence of clay nor nanocomposite formation has an effect on the degradation pathway of HIPS.

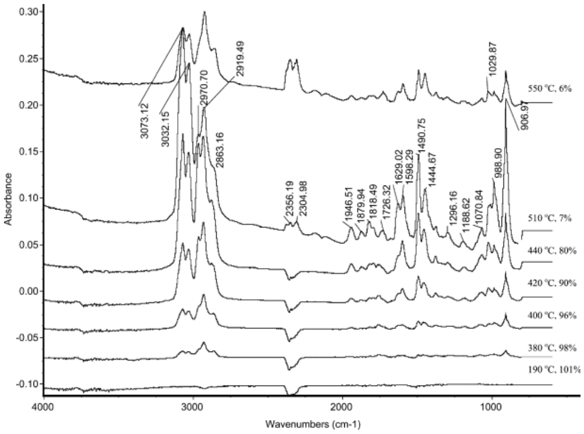

Fig. 9. FT-IR spectra from a TGA/FTIR study of COPS/HIPS nanocomposite.

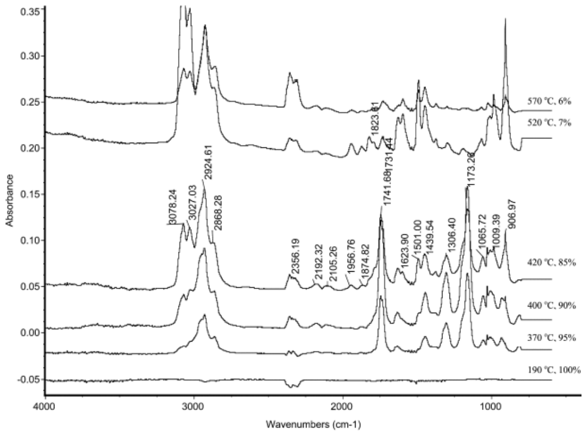

Fig. 10. FT-IR spectra from a TGA/FTIR study of MAPS/HIPS nanocomposite.

3.4. Thermal degradation of ABS and its COPS and MAPS nanocomposites

It has been reported [8] that the first band seen in ABS degradation is due to butadiene. This is not seen in this study but one can clearly see the degradation of the styrene portion from the C–H stretching frequency, as shown in Fig. 11. There is a brief hint of a nitrile peak, on the edge of the carbonyl peak, as previously reported [8]. Both monomer and oligomer are produced in about equal amounts. The TGA curves of ABS and both nanocomposites are shown in Fig. 12; there is not a great difference in thermal stability amongst the three systems shown but both COPS–ABS and MAPS–ABS show slightly enhanced thermal stability.

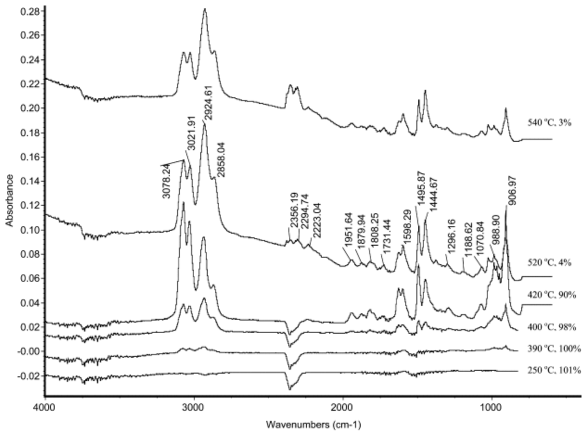

Fig. 11. FT-IR spectra from a TGA/FTIR study of virgin ABS.

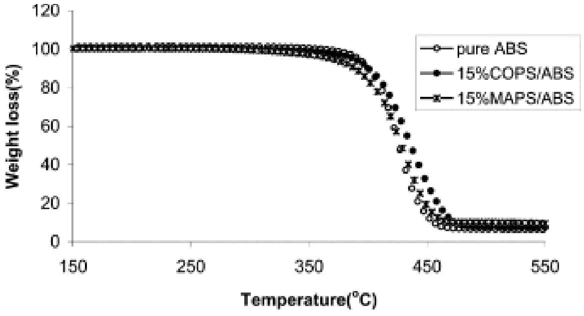

Fig. 12. TGA curves for ABS and its COPS and MAPS nanocomposites.

The COPS–ABS, shown in Fig. 13, nanocomposite seems to begin degradation at a slightly lower temperature than does the pure polymer. It is of interest to note that monomer and oligomer are evolved in about equal amounts at the beginning of the degradation but monomer is decreased and mostly oligomer is obtained at 540 °C; this same behavior is seen for virgin ABS. The thermal degradation of MAPS–ABS (Fig. 14) begins at much lower temperature, due to methacrylate degradation. The presence of aromatic C–H is not seen at 360 °C but this is evident at a somewhat higher temperature. In the initial stage of styrenic degradation, mainly monomer is observed but oligomer is evolved at higher temperatures and it becomes the dominant species at the highest temperatures. Once again, no difference in the evolved gases are observed for the virgin polymer, a mixed intercalated/exfoliated nanocomposite (COPS) and a microcomposite (MAPS).

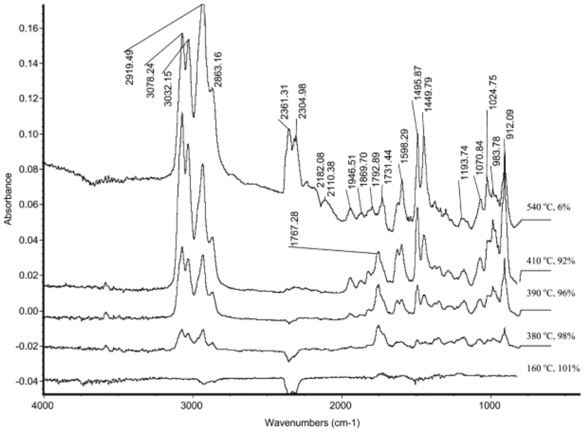

Fig. 13. FT-IR spectra from a TGA/FTIR study of COPS/ABS nanocomposite.

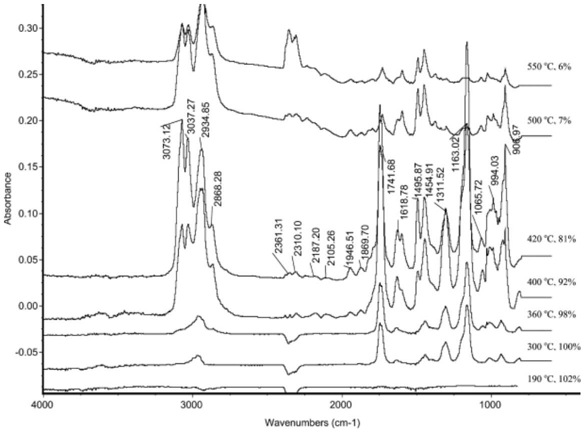

Fig. 14. FT-IR spectra from a TGA/FTIR study of MAPS/ABS nanocomposite.

3.5. Thermal degradation of PMMA and its COPS and MAPS nanocomposites

Kashiwagi has shown that PMMA shows three distinct degradation steps when a thermogravimetric analysis is run at a rate of 1–2 °C per minute. We have previously reported that one may also see these steps at 10 °C per minute in a nanocomposite. The TGA traces of pure PMMA and its COPS and MAPS nanocomposite, which illustrate this, are shown in Fig. 15; the presence of the multiple steps can be seen most clearly in COPS–PMMA. One may state that the observation of multiple steps in the degradation, which is not seen in virgin PMMA except at very low heating rates, may involve a templating effect, following the ideas of Blumstein that have been discussed above.

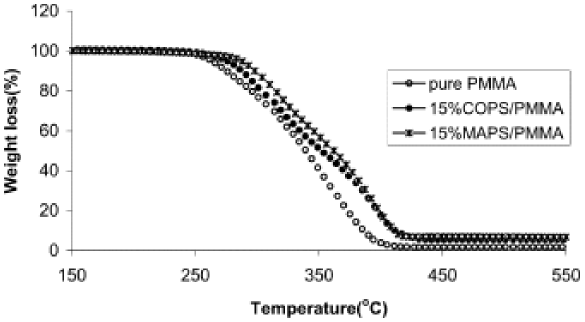

Fig. 15. TGA curves for PMMA and its COPS and MAPS nanocomposites.

The first comparison that will be made here is between virgin PMMA, shown in Fig. 16, and the MAPS nanocomposite (Fig. 3). It is obvious that the evolution of carbonyl begins earlier in pure PMMA, about 230 °C, than in MAPS, about 250 °C. This enhanced stability may be attributable to the separation between MMA units. The spectra of the gases that evolve from the COPS–PMMA and MAPS–PMMA nanocomposites, shown in Fig. 17, Fig. 18, respectively, show that the degradation commences at about 230 °C, in the same region that PMMA undergoes degradation. Nanocomposite formation does not have a significant effect on the evolved gases from PMMA degradation.

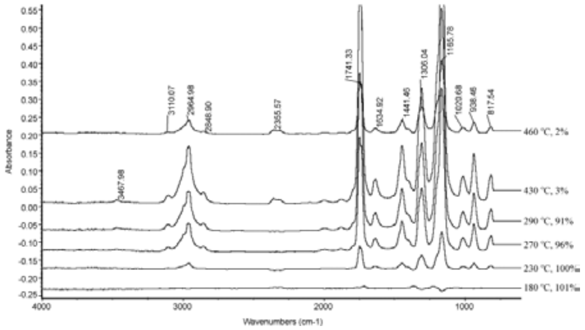

Fig. 16. FT-IR spectra from a TGA/FTIR study of virgin PMMA.

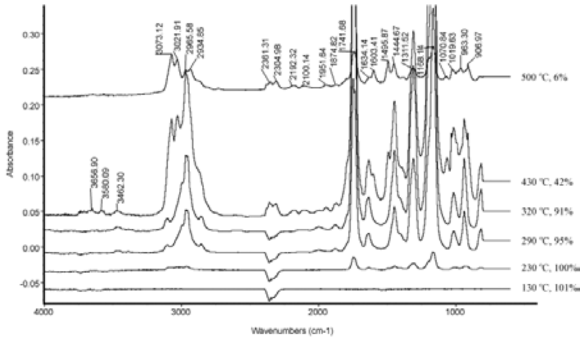

Fig. 17. FT-IR spectra from a TGA/FTIR study of COPS/PMMA nanocomposite.

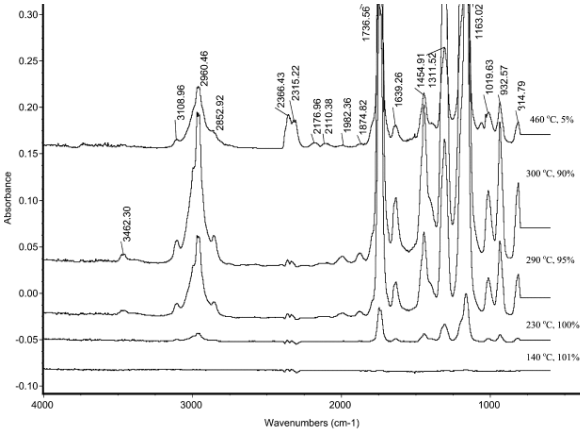

Fig. 18. FT-IR spectra from a TGA/FTIR study of MAPS/PMMA nanocomposite.

3.6. Thermal degradation of polypropylene and its COPS and MAPS nanocomposites

In the spectra of virgin PP, shown in Fig. 19, one can see bands that can be assigned, in agreement with the literature [21], to the formation of an alkene mixture, corresponding to peaks at 3073, 2960, 2914,1644,1373, and 866 cm^{-1}. The TGA curves, shown in Fig. 20, show that the onset of the degradation is a little higher for the COPS–PP system, while the MAPS–PP system is a little more stable at the end of the degradation. A similar set of infrared peaks are observed in both COPS–PP (Fig. 21) and MAPS–PP (Fig. 22). The temperature at which these peaks first appear is somewhat higher for COPS–PP and unchanged for MAPS–PP, in agreement with the TGA curves.

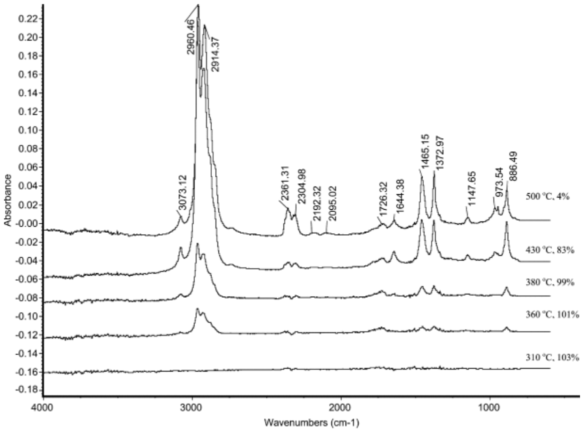

Fig. 19. FT-IR spectra from a TGA/FTIR study of virgin polypropylene.

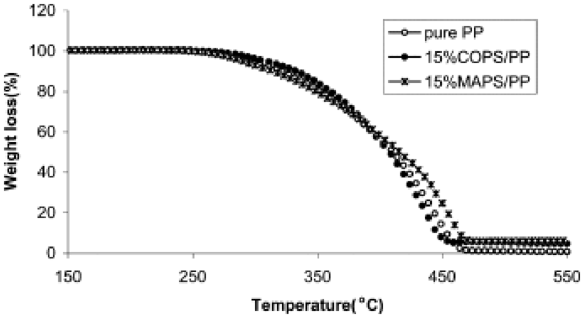

Fig. 20. TGA curves for PP and its COPS and MAPS nanocomposites.

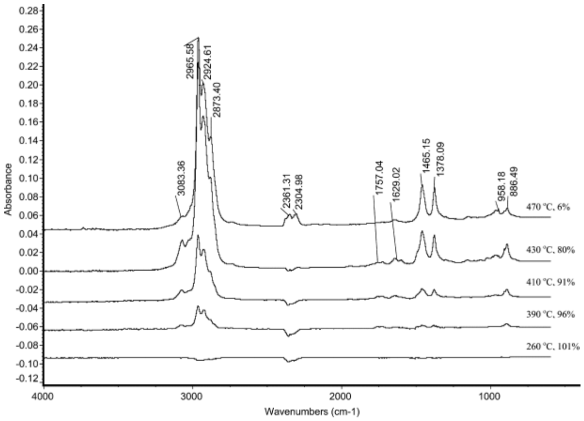

Fig. 21. FT-IR spectra from a TGA/FTIR study of COPS/PP nanocomposite.

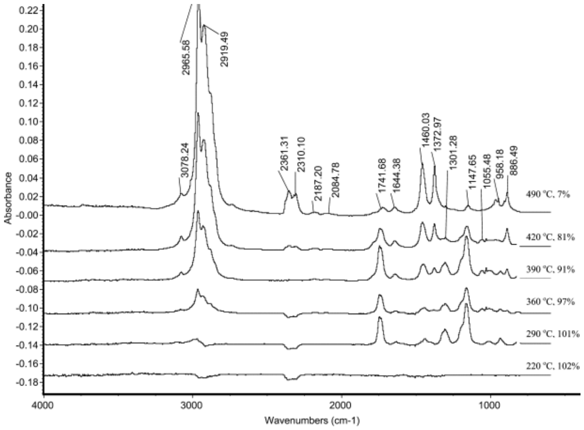

Fig. 22. FT-IR spectra from a TGA/FTIR study of MAPS/PP nanocomposite.

3.7. Thermal degradation of polyethylene and its COPS and MAPS nanocomposites

The degradation of polyethylene occurs by random scission, commencing at about 400 °C and is complete by 500 °C [22], [23]. In this study, the spectra of virgin PE commence at about 400 °C but the evolution of gases, primarily olefins, continues above 500 °C, as shown in Fig. 23. The TGA curves, shown in Fig. 24, are quite similar to those of polyethylene. The COPS nanocomposite has somewhat higher thermal stability at lower temperatures while the MAPS–PE system undergoes degradation at higher temperatures in the middle region of the degradation. If one ignores the clay degradation that occurs when using MAPS, the results are identical for both COPS-PE (Fig. 25) and MAPS–PE (Fig. 26).

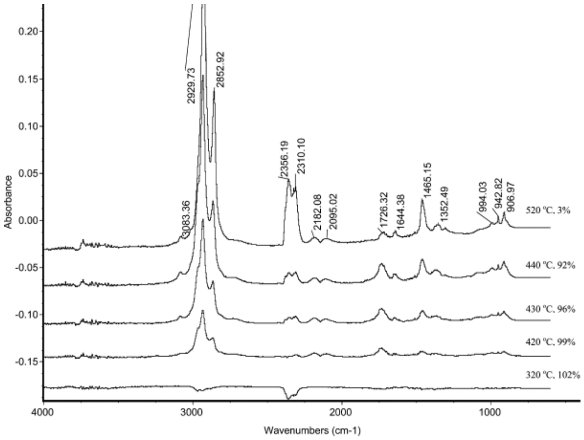

Fig. 23. FT-IR spectra from a TGA/FTIR study of virgin polyethylene.

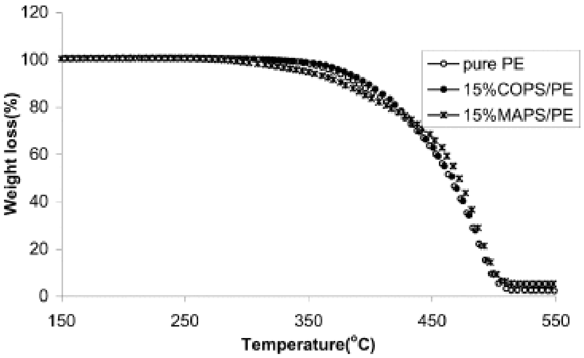

Fig. 24. TGA curves for PE and its nanocomposites.

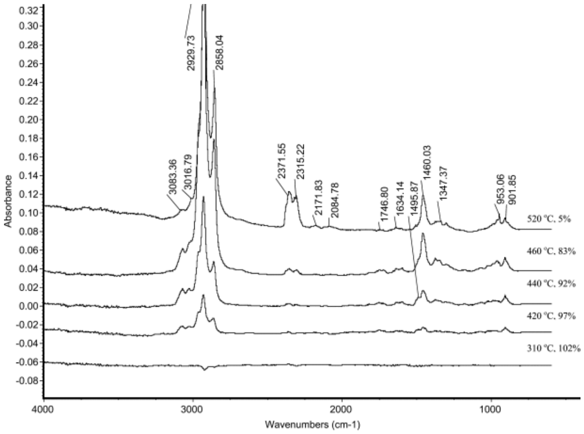

Fig. 25. FT-IR spectra from a TGA/FTIT study of COPS/PE nanocomposite.

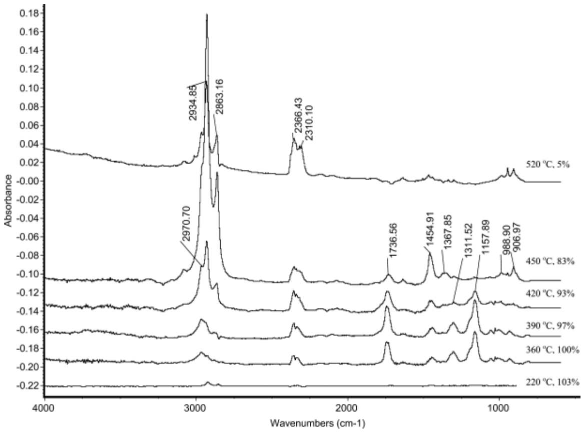

Fig. 26. FT-IR spectra from a TGA/FTIR study of MAPS/PE nanocomposite.

4. Conclusions

The presence of clay, whether in the form of a nanocomposite or a microcomposite, has no effect on the evolved gases during the degradation of the materials, except in very limited cases. It is evident that the presence of the clay has an effect in the degradation of styrenics because peaks that may be attributable to oligomer are observed while those due to monomer are absent when clay is present. This observation may explain why the peak heat release rate in a cone calorimetry experiment shows a different reduction for different polymers. In the case of polystyrene, the monomer must be more volatile than are oligomers and thus must be able to escape to the gas phase more easily and burn. If one can reduce the fraction of monomer, the amount of fuel that is easily produced will decrease and the heat release curve must change. Based on this work, the role of the clay in styrenics polymers is to change the ratio of monomer to oligomer, in favor of oligomer. One can generalize from this and suggest that for polymers which degrade by a process that produces a mixture of monomer and oligomer, one can expect to see a large change in the heat release rate curve. For polymers, such as poly(methyl methacrylate), which degrade to produce only, or mainly, monomer, the change in the curve (and the reduction in peak heat release rate) will not be large.

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